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Dependence of chemical composition of styrene/butyl acrylate copolymers on temperature and molecular weight

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Abstract

The temperature dependence of the reactivity ratios of the system styrene/butyl acrylate is studied. Copolymers of styrene and butyl acrylate are therefore synthesised in bulk at 50, 90, 100 and 120°C. Copolymer composition is determined by ^{1}H NMR, the resulting data are evaluated, and Arrhenius parameters are obtained for r_{BA}. In order to investigate the molecular-weight dependence of the copolymer composition, copolymerisations of styrene and butyl acrylate are carried out at 50 and 90°C in the presence of mercapto ethanol. No molecular-weight dependence is found for the investigated system. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Reactivity ratios; Copolymers; Temperature dependence

1. Introduction

An important aspect of copolymerisation is the chemical composition of the copolymers formed and how this chemical composition can be explained in terms of a copolymerisation mechanism. The investigation of copolymerisation of polar and hydrogen bonding comonomer pairs has attained great interest over the years, since they often do not obey simple copolymerisation models.

Harwood et al. [1] investigated the influence of various solvents on the copolymerisation kinetics of a comonomer pair that consisted of a polar and a non-polar monomer. These copolymerisations in different solvents lead to different overall chemical composition and thus to different sets of reactivity ratios. However, they found that copolymers with the same overall chemical composition also had the same sequence distribution, i.e. the same microstructure. Harwood ascribed this phenomenon to a different ratio of comonomers in the vicinity of the polymer radical as compared to the global ratio and called it the ‘bootstrap’ effect. The model implies that a growing polymer radical is actually able to control its own environment.

Semchikov et al. [2] investigated the molecular-weight dependence of copolymer composition for a number of systems. By fractionating his polymer samples, he was able to conclude that for many of these systems the incorporation of both monomers changes during polymer growth. This phenomenon was explained by preferential sorption, i.e. the polymer coil is able to adsorb one of the monomers preferentially, thus causing a different comonomer ratio as compared to the global comonomer ratio.

O’Driscoll [3] theoretically evaluated the temperature dependence of reactivity ratios. For a copolymerisation of monomer 1 with monomer 2, the r_1 can be written as follows:

$$r_1 = \frac{k_{11}}{k_{12}} = \frac{A_{11}\cdot e^{\frac{-E_{11}}{RT}}}{A_{12}\cdot e^{\frac{-E_{12}}{RT}}} \tag{1}$$

The expression for r_1 is an Arrhenius type equation itself. O’Driscoll then assumes that $A_{11} \approx A_{12}$, and eventually the following expression is obtained:

$$\frac{d(\ln r_1)}{d(1/T)} = T\cdot\ln r_1 \tag{2}$$

An analogous expression can be derived for r_2. O’Driscoll concludes from Eq. (2) that reactivity ratios tend to go to unity when temperature is increased.

This paper investigates the copolymerisation kinetics of the system styrene/butyl acrylate (Sty/BA). According to Semchikov et al. [4], this system, which obeys the terminal model [5,6], shows a molecular-weight dependence of chemical composition. Furthermore, reactivity ratios of this system will be evaluated at different temperatures to

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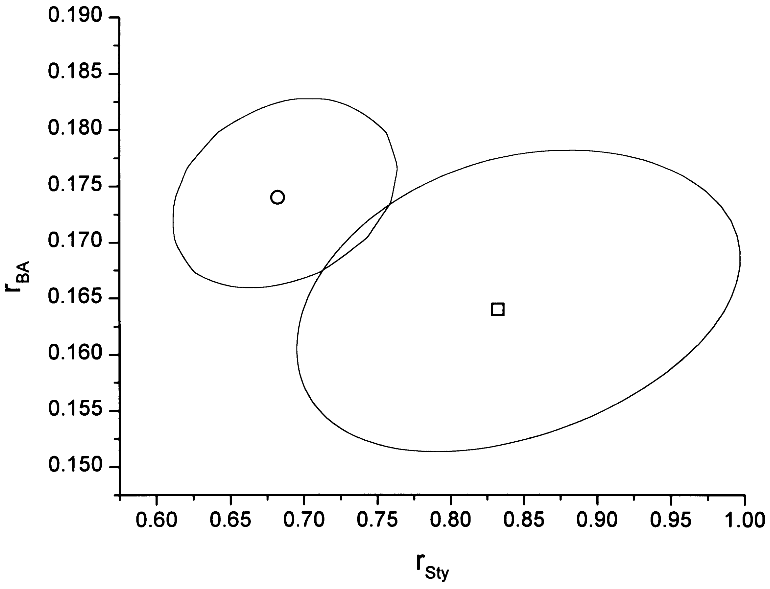

Fig. 1. 95% joint confidence intervals of the terminal model reactivity ratios of the copolymerisation of styrene and butyl acrylate at 50°C in bulk without CTA (□, $r_{Sty} = 0.832$; $r_{BA} = 0.164$) and with CTA (○, $r_{Sty} = 0.682$; $r_{BA} = 0.174$).

check whether they obey the theory that they should go towards unity when temperature is increased. Reactivity ratios at elevated temperatures are gaining interest due to the high temperature ranges at which nitroxide-mediated controlled radical polymerisation is carried out.

2. Experimental

Prior to use, styrene ($>$ 99% stabilised by 4-*tert*-butylcatechol, Merck) and butyl acrylate ($>$ 99% stabilised by monomethyl ether hydroquinone, Aldrich) were distilled under reduced pressure and subsequently passed through a column too remove residual inhibitor. An appropriate inhibitor replacement packing (Aldrich) was used for each monomer. 2,2′-Azobis(isobutyronitrile) (AIBN) was recrystallised once in methanol. All other chemicals were used as received.

Styrene/butyl acrylate copolymers were prepared at 50, 90, 100 and 120°C in bulk. For the investigation of molecular-weight dependence of copolymer composition, copolymerisations were also carried out in the presence of a chain transfer agent, viz. mercapto ethanol.

Optimal monomer feed compositions were calculated applying the Tidwell–Mortimer criterion and using literature values of the reactivity ratios. At both optimal feed ratios, five copolymerisations were carried out. Conversion was determined gravimetrically and was kept below 1% in most cases. Thereafter, the reaction mixtures were freeze-dried and subsequently dried in a vacuum oven at room temperature for 1 day.

Copolymer composition was determined by ^{1}H NMR on a 400 MHz Bruker at 50°C in $CDCl_3$. Peak areas of the proton resonances at 7 ppm (phenyl) and 3.8 ppm (methoxyl) were taken to calculate copolymer composition. Monomer feed versus copolymer composition data were evaluated using non-linear least squares fitting which yields the most accurate values of both reactivity ratios [7,8]. No alternative methods were tested. Molecular weights were determined by size exclusion chromatography with tetrahydrofuran as eluent at 25°C. Polystyrene standards from Polymer Laboratories were used for calibration.

3. Results and discussion

3.1. Molecular-weight dependence of reactivity ratios

At 50°C copolymerisations yield polymers having molecular weights (M_w) up to 1×10^6 g/mol, while those obtained in copolymerisations with CTA have molecular weights which do not exceed 2×10^4 g/mol. However, when looking at Fig. 1, these large differences in molecular weights do not lead to large differences in reactivity ratios. These small differences can be explained by looking at the propagation rate constants for both cases. It is known that propagation rate constants are chain-length dependent [9]. However, the propagating radicals might be affected to a different extent, resulting in different copolymer composition at short chain lengths. The difference in observed reactivity ratios originates, therefore, from a difference in chain-length dependence of both propagation rate constants. This effect could well be an explanation for the small differences in reactivity ratios in the case of the copolymerisations at 50°C, where the short copolymers had a chain length of approximately 20 monomer units.

At 90°C no difference in reactivity ratios can be observed, although molecular weights differ by a factor of 5 to 10.

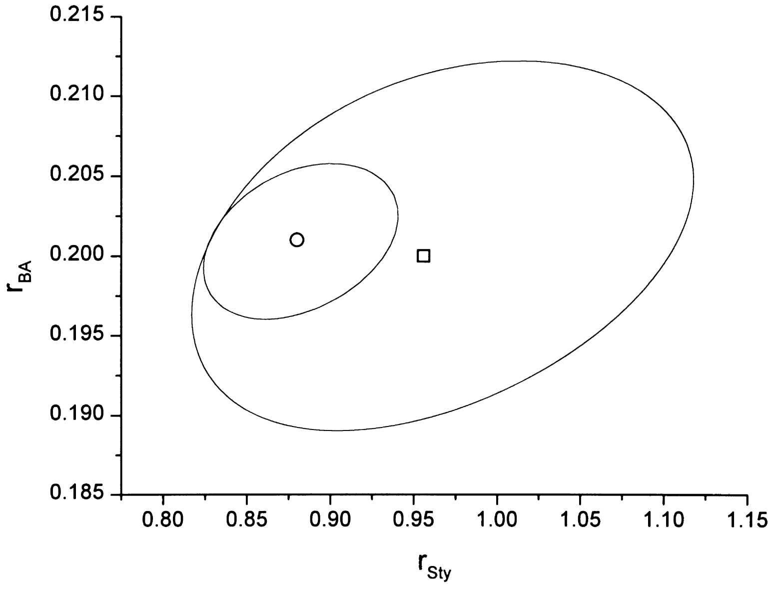

Fig. 2. 95% joint confidence intervals of the terminal model reactivity ratios of the copolymerisation of styrene and butyl acrylate at 90°C in bulk without CTA (□, $r_{Sty} = 0.956$; $r_{BA} = 0.200$) and with CTA (○, $r_{Sty} = 0.88$; $r_{BA} = 0.201$).

This is depicted in Fig. 2 where the 95% joint confidence intervals of both sets of reactivity ratios completely overlap.

The differences in 95% joint confidence intervals of the copolymerisations in the presence of chain-transfer agent in Figs. 1 and 2 are much larger than those of the copolymerisations without chain-transfer agent. This, however, is not a systematic phenomenon, but is a result of random differences in the data structure.

3.2. Temperature dependence of reactivity ratios

From Fig. 3 it seems that initially the reactivity ratios indeed go towards unity with increasing temperature. However, at 120°C r_{BA} is still increasing, while r_{Sty} has dropped to a value of 0.81. But, if a closer look is cast on the confidence intervals for r_{Sty} it seems that they all overlap and, as a consequence, that they can all be regarded as one value already close to unity.

When taking a closer look at r_{BA}, it can be written according to Eq. (1) as:

$$r_{BA} = \frac{A_{BABA}}{A_{StyBA}} \cdot e^{-\frac{(E_a^{BABA} - E_a^{StyBA})}{RT}} \tag{3}$$

Since r_{BA} is nothing more than a ratio of propagation rate

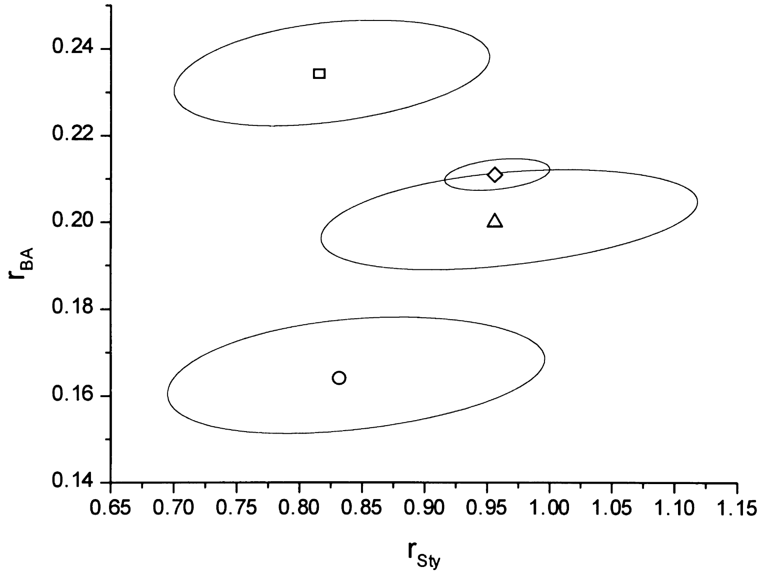

Fig. 3. 95% joint confidence intervals of the terminal model reactivity ratios of the copolymerisation of styrene and butyl acrylate at 50°C (○), 90°C (△), 100°C (◇) and 120°C (□).

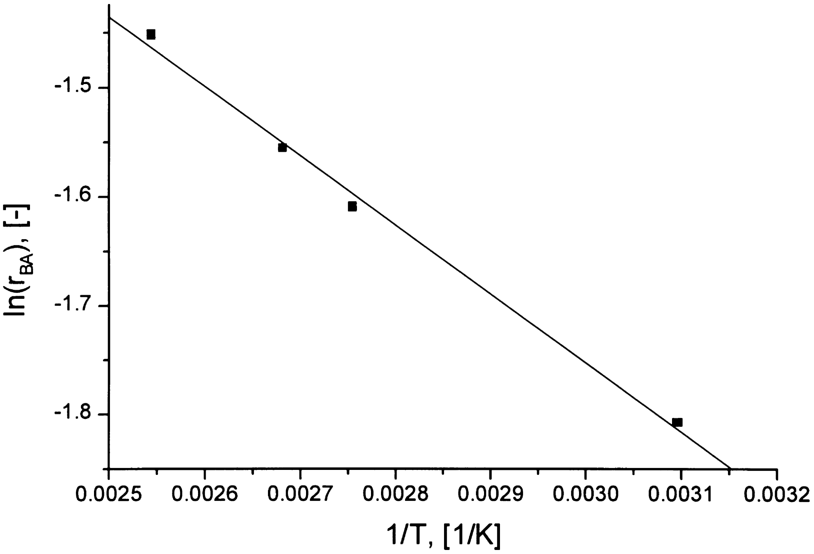

Fig. 4. Temperature dependence of r_{BA} where $\ln(A_{\mathrm{BABA}}/A_{\mathrm{BASty}}) = 1.16$ and $(E_a^{\mathrm{BABA}} - E_a^{\mathrm{StyBA}})/R = 634$ K.

constants, it is possible to draw an Arrhenius plot for the temperature dependence of r_{BA}.

From Fig. 4 it follows that $\ln(A_{\mathrm{BABA}}/A_{\mathrm{BASty}}) = 1.16$ and it can be concluded that this factor is indeed fairly small and can be omitted in the derivation that O'Driscoll has put forward. The slope of the Arrhenius plot is the difference in activation energies of homo- and cross-propagation divided by the gas constant ($R = 8.314$ J/mol·K) and equals 634 K, which corresponds to 5.27 kJ/mol. The slope of the Arrhenius plot can also be calculated for each r_{BA} value according to Eq. (2). However, if these values are compared with the one from the Arrhenius plot, it is clear that the calculated values are consequently too low (see Table 1).

This inconsistency can be explained by doing the same derivation as stated above, but not neglecting the pre-exponential factor for homo- and cross-propagation:

$$r_1 = \frac{A_{11}}{A_{12}} \cdot e^{\frac{E_{\mathrm{BABA}} - E_{\mathrm{BASty}}}{RT}}$$

$$\ln(r_1) = \ln\left(\frac{A_{11}}{A_{12}}\right) - \frac{E_{\mathrm{BABA}} - E_{\mathrm{BASty}}}{RT}$$

When assuming no temperature dependence in the ratio of the pre-exponential factors, Eq. (2) can be written as follows:

$$\frac{d(\ln r_1)}{d(1/T)} = T \cdot \left(\ln r_1 - \ln\left(\frac{A_{11}}{A_{12}}\right)\right) \tag{4}$$

From Eq. (4) it can be seen that in order to calculate the slope of the linearised Arrhenius equation from individual (T, r_{BA}) data points, the ratio of pre-exponential factors of homo- and cross-propagation has to be known beforehand.

Table 1
Calculated slope according to Eq. (2)

Temperature (K)	r_{BA} (−)	Slope calculated (K)
232	0.164	584
363	0.20	584
373	0.211	580
393	0.234	571

4. Conclusions

For the system styrene/butyl acrylate, a small molecular-weight dependence could be detected at 50°C. However, molecular weights ranged from 10^4 to 10^6 g/mol and therefore the origin of this molecular-weight dependence can be explained by differences in propagation rate constants at short chain length.

The fact that Semchikov et al. also found a dependence for higher molecular-weight copolymers could perhaps be explained by the experimental procedures used. First, in contrast to our procedure, the copolymers were purified in appropriate solvents assuming separation on the basis of molecular weight. Separation of the copolymers, however, could also have occurred on the basis of chemical composition, and thus the resulting reactivity ratios are less reliable. Furthermore, conversion in the work of Semchikov et al. was usually 5–7%, in contrast to this work, where conversion was kept below 1% in most cases. Evaluation of the temperature dependence of r_{BA} yields the parameters for cross-propagation. By using data for homo-propagation of butyl acrylate [10], it is possible to derive the kinetic parameters for the cross-propagation. When E_{BABA} is taken as 17.3 kJ/mol, it can be calculated that $E_{\mathrm{BASty}} = 22.6$ kJ/mol. When E_{BABA} is taken as 1.58×10^7 L/mol·s and using $\ln(A_{\mathrm{BABA}}/A_{\mathrm{BASty}}) = 1.16$, then $A_{\mathrm{BASty}} = 4.95 \times 10^6$.

Finally, r_{BA} seems to obey the theory that reactivity ratios tend toward unity when temperature is increased.

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